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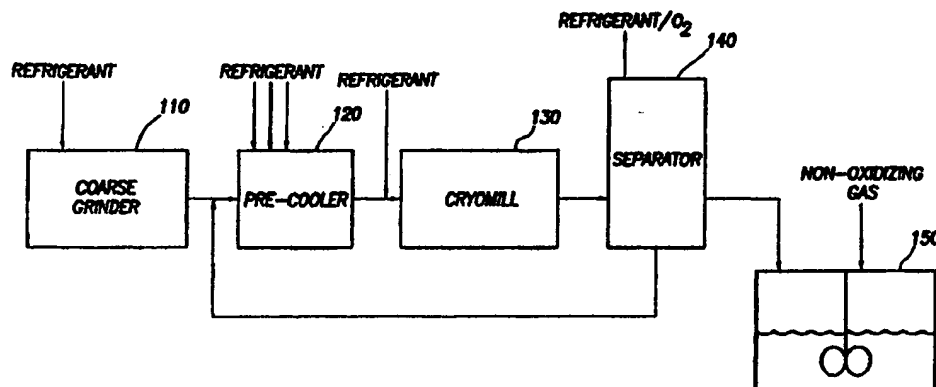
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(54) Title: DRAG-REDUCING POLYMER SUSPENSIONS



(57) Abstract: A hydrocarbon-soluble drag-reducing suspension is described, along with a process for manufacturing the drag-reducing suspension. The drag-reducing suspension is easily transportable, non-hazardous, easily handled, and provides a significant increase in drag-reducing capability over existing products. The drag-reducing suspension is manufactured by grinding an ultra-high molecular weight polymer in the presence of a grinding aid and mixing it with a suspending fluid.

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DRAG-REDUCING POLYMER SUSPENSIONS

The present invention relates to drag-reducing polymer suspensions and their method of manufacture. More specifically, this invention relates to a method for preparing
5 an ultra-high molecular weight, substantially non-crystalline hydrocarbon soluble polymer suspension.

A drag-reducing agent is one that substantially reduces the friction loss that results from the turbulent flow of a fluid. Where fluids are transported over long distances, such as in oil and other hydrocarbon liquid pipelines, these friction losses result in inefficiencies
10 that increase equipment and operations costs. Ultra-high molecular weight polymers are known to function well as drag-reducing agents, particularly in hydrocarbon liquids. In general, drag reduction depends in part upon the molecular weight of the polymer additive and its ability to dissolve in the hydrocarbon under turbulent flow. Effective drag-reducing polymers typically have molecular weights in excess of five million.

15 Drag-reducing polymers are known in the art. Representative, but non-exhaustive, samples of such art are: U.S. Pat. No. 3,692,676, which teaches a method for reducing friction loss or drag for pumpable fluids through pipelines by adding a minor amount of a high molecular weight, non-crystalline polymer; and U.S. Pat. No. 3,884,252, which teaches the use of polymer crumb as a drag-reducing material. These materials are
20 extremely viscoelastic and, in general, have no known use other than as drag-reducing materials. However, the very properties that make these materials effective as drag-reducing additives make them difficult to handle because they have a severe tendency to cold flow and reagglomerate even at subambient temperatures. Under conditions of pressure, such as stacking or palleting, cold flow is even more intense and reagglomeration
25 occurs very quickly.

The general propensity of non-crosslinked elastomeric polymers (elastomers) to cold flow and agglomerate is well-known. Polymers of this sort cannot be pelletized or put into discrete form and then stored for any reasonable period of time without the materials flowing together to form large agglomerates. Because of such difficulties, elastomers are normally shipped and used as bales. However, such bales must be handled on expensive equipment and cannot be pre-blended. In addition, polymers such as the drag-reducing additives described are not susceptible to such balings, since cold flow is extremely severe. Further, dissolution time for such drag-reducing materials from a polymer state in the flowing hydrocarbons to a dissolved state is so lengthy as to severely reduce the effectiveness of this material as a drag-reducing substance.

Numerous attempts have been made to overcome the disadvantages inherent in cold-flowing polymers. Representative, but non-exhaustive, of such art is that described in U.S. Pat. No. 3,791,913, wherein elastomeric pellets are surface cured, *i.e.*, vulcanized to a minor depth in order to maintain the unvulcanized interior of the polymer in a "sack" of cured material, and U.S. Pat. No. 4,147,677, describing a method of preparing a free-flowing, finely divided powder of neutralized sulfonated elastomer by admixing with fillers and oils. This reference does not teach a method for making free-flowing powders of non-elastomeric material. U.S. Pat. No. 3,736,288 teaches solutions of drag-reducing polymers in inert, normally liquid vehicles for addition to liquids flowing in conduits. A "staggered dissolution" effect is provided by varying the size of the polymer particles. Suspension or surface-active agents can also be used. While directed to ethylene oxide polymers, the method is useful for hydrocarbon-soluble polymers as well. U.S. Pat. No. 4,088,622 describes a method of making an improved, molded drag-reducing coating by incorporating

antioxidants, lubricants, and plasticizers and wetting agents in the form of a coating which is bonded directly onto the surface of materials passing through a liquid medium. U.S. Pat. No. 4,340,076 teaches a process for dissolving ultra-high molecular weight hydrocarbon polymer and liquid hydrocarbons by chilling to cryogenic temperatures comminuting the polymer formed into discrete particles and contacting these materials at near cryogenic temperatures with the liquid hydrocarbons to more rapidly dissolve the polymer. U.S. Pat. No. 4,341,078 immobilizes toxic liquids within a container by injecting a slurry of cryogenically ground polymer particles while still at cryogenic temperatures into the toxic liquid. U.S. Pat. No. 4,420,440 teaches a method for collecting spilled hydrocarbons by dissolving sufficient polymer to form a nonflowing material of semisolid consistency by contacting said hydrocarbons with a slurry of cryogenically comminuted ground polymer particles while still at cryogenic temperatures.

Some current drag-reduction systems inject a drag-reducing polymer solution containing a high percentage of dissolved, ultra-high molecular weight polymer into conduits containing the hydrocarbon. The drag-reducing polymer solution is normally extremely thick and difficult to handle at low temperatures. Depending upon the temperature of the hydrocarbon and the concentration at which the drag-reducing polymer solution is injected, significant time elapses before dissolution and resulting drag reduction.

Solid polymers of these types can take days to dissolve in some cases, even though drag reduction is greatly enhanced once dissolution has finally occurred. Also, such ultra-high molecular weight polymer solutions become very viscous as polymer content increases, in some cases limiting the practical application of these solutions to those containing no more than about 15 weight percent polymer. This makes complex equipment necessary for

storing, dissolving, pumping, and injecting metered quantities of drag-reducing material into flowing hydrocarbons.

Another way to introduce ultra-high molecular weight polymers into the flowing hydrocarbon stream is through a suspension. The ultra-high molecular weight polymers are suspended in a liquid that will not dissolve or will only partially dissolve the ultra-high molecular weight polymer. This suspension is then introduced into the flowing hydrocarbon stream. The tendency of the ultra-high molecular weight polymers to reaggregate makes manufacture of these suspensions difficult. A way of controlling the tendency of the ultra-high weight polymers to reaggregate is to partially surround the polymer particles with a partitioning agent, occasionally termed a coating material, to reduce the ability of these polymers to reaggregate. U.S. Pat. No.4,584,244, which is hereby incorporated by reference, describes a process whereby the polymer is ground and then coated with alumina to form a free-flowing powder. Other examples of partitioning agents used in the art include talc, tri-calcium phosphate, magnesium stearate, silica, polyanhydride polymers, sterically hindered alkyl phenol antioxidants, and graphite. Some processes using a partitioning agent such as those described in U.S. Patent Nos. 4,720,397, 4,826,728, and 4,837,249 require that the partitioning agent be surrounded with multiple layers of a partitioning agent to protect the core from exposure to water and oxygen. Experience has shown that this most often requires a vast amount of partitioning agent, and is rarely effective as a partitioning agent typically will not stick to itself. Further, the composition created by these processes would have dissolution problems, as the hydrocarbon would be unable to reach the polymer core that would be insulated by the layers of partitioning agent. Additionally the processes described in these patents require

that the polymer be coated with the partitioning agent while within an inert atmosphere, *i.e.*, one that is free from oxygen and water. This requires special, vapor-tight equipment that is expensive to maintain.

What is needed is a process for manufacturing a drag-reducing agent that does not
5 require an inert environment and huge amounts of partitioning agent. The composition should be easily dissoluble in the hydrocarbon. Finally, the composition should be suspended in a fluid for easy transport and injection into the hydrocarbon.

Accordingly, a drag-reducing suspension and a method of producing a drag-reducing suspension are disclosed herein. One embodiment of the present invention is
10 drawn to a method for the preparation of a drag-reducing polymer suspension wherein an ultra-high molecular weight polymer is mixed with a grinding aid to form a polymer/grinding aid mixture. This mixture is then ground at a temperature below the glass transition temperature of the ultra-high molecular weight polymer to form ground polymer/grinding aid particles. The ground polymer/grinding aid particles are then mixed
15 with a suspending liquid to form the drag-reducing polymer suspension. In another embodiment of the present invention, drag-reducing polymer suspension is prepared by cooling an ultra-high molecular weight polymer with nitrogen, helium, argon, or dry ice.

The ultra-high molecular weight polymer is a linear poly(α -olefin) comprised of monomers with carbon chain lengths of between 4 and 20 carbons. The ultra-high
20 molecular weight polymer is mixed with a grinding aid to form a polymer/grinding aid mixture. This mixture is then ground at a temperature below the glass transition temperature of the ultra-high molecular weight polymer. The mixture is then mixed with

a suspending fluid. At least one of the following components is then added to the suspending fluid: wetting agent, antifoaming agent, and thickening agent.

One advantage of the present invention is that the drag-reducing polymer suspension is easily transportable and does not require pressurized or special equipment for storage, transport, or injection. Another advantage is that the drag-reducing polymer is quickly dissolved in the flowing hydrocarbon stream. Yet another advantage of the present invention is that the extra bulk and cost associated with the inert coating agent may be eliminated, allowing easier transport. Still another advantage of the present invention is that reagglomeration of the drag-reducing polymers is greatly reduced, allowing for easier handling during manufacture. Another advantage of the present invention is that the drag-reducing polymer suspension is stable, allowing a longer shelf life and balancing of customer demand with manufacturing time. A further advantage of the present invention is that the amount of inert ingredients in the final product is reduced. In addition, manufacturing throughput is increased by the use of the grinding aid.

Figure 1 is a schematic of the apparatus for manufacturing the drag-reducing polymer suspension.

In the present invention, ultra-high molecular weight polymers are ground at temperatures below the glass transition temperature of the polymer or polymer blends, and then mixed in a suspending fluid. These polymers are generally not highly crystalline. An ultra-high molecular weight polymer typically has a molecular weight of greater than 1 million, preferably more than 5 million. Glass transition temperatures vary with the type of polymer, and typically range between -10°C and -100°C (14°F and -148°F). This temperature can vary depending upon the glass transition point of the particular polymer

or polymer blend, but normally such grinding temperatures must be below the lowest glass transition point of any polymer that comprises a polymer blend.

A preferred ultra-high molecular weight polymer is typically a linear poly(α -olefin) composed of monomers with a carbon chain length of between four and twenty carbons or mixtures of two or more such linear poly(α -olefins). Typical examples of these linear poly(α -olefins) include, but are not limited to, poly(1-octene), poly(1-decene) and poly(1-dodecene). The ultra-high molecular weight polymer may also be a copolymer, *i.e.*, a polymer composed of two or more different types of monomers, as long as all monomers used have a carbon chain length of between four and twenty carbons. Other polymers of a generally similar nature that are soluble in the liquid hydrocarbon will also function in the invention.

As shown in Figure 1, the ultra-high molecular weight polymer is conveyed to coarse chopper 110. Coarse chopper 110 chops large chunks of polymer into small polymer pieces, typically between 0.5 to 1.75 centimeters (1/4 inch to 5/8 inch) in diameter. While coarse chopper 110 may be operated at ambient temperatures, it is preferable to cool the polymer in coarse chopper 110 to less than 30°C (85°F) between 5°C to 15°C (41°F to 59°F). The polymer in coarse chopper 110 may be cooled either internally or externally or both, with a liquid gaseous or solid refrigerant or a combination thereof, but most commonly by spraying a liquid refrigerant into coarse-chopper 110, such as liquid nitrogen, liquid helium, liquid argon, or mixtures of two or more such refrigerants. It may be advantageous to pre-cool coarse chopper 110 prior to introduction of the polymer. The pre-cooling may be accomplished by methods similar to those used for cooling the polymer in coarse chopper 110. A small amount of a partitioning agent, typically less than about

10% and preferably less than about 8% by weight of the total mixture, may be used in coarse chopper 110 in order to prevent agglomeration of the small polymer pieces. Partitioning agents include calcium stearate, alumina, talc, clay, tri-calcium phosphate, magnesium stearate, polyanhydride polymers, sterically hindered alkyl phenol oxidants, graphite, and various stearamides. Partitioning agents should be compatible with the hydrocarbon fluid and should be non-reactive or minimally reactive with the polymer, suspending fluid, and grinding aid. Individual particles of the partitioning agent added to coarse chopper 110 must be small enough to reduce re-agglomeration of the small polymer pieces to an acceptable level. Typically, the particles of the partitioning agent added to coarse chopper 110 are coarse to fine-sized, able to pass through a 140 mesh screen.

Coarse chopper 110 need not be vapor-tight and the atmosphere within coarse chopper 110, while typically enriched in the refrigerant from the cooling process, normally contains substantial oxygen and water vapor from the ambient air.

The small pieces of polymer and partitioning agent formed in coarse chopper 110 are then transported to pre-cooler 120. This transport may be accomplished by any number of typical solids handling methods, but is most often accomplished through the use of an auger or a pneumatic transport system. Pre-cooler 120 may be an enclosed screw conveyor with nozzles for spraying a liquid refrigerant, such as liquid nitrogen, helium, argon, or mixtures thereof, onto the small polymer pieces. Like coarse chopper 110, pre-cooler 120 is often not vapor-tight and contains oxygen and water vapor present in the ambient air.

While a gaseous refrigerant may also be used alone, the cooling efficiency is often too low. A grinding aid is added to the ultra-high molecular weight polymer prior to cooling in pre-cooler 120. A preferred grinding aid is a material with a melting point of between

-100°C to 25°C (-148°F to 77°F), or a material that is totally soluble in the suspending fluid under the conditions disclosed herein when the suspension is produced in mixing tank 150. Examples of grinding aids include ice (frozen water), sucrose, glucose, lactose, fructose, dextrose, sodium saccharin, aspartame, starches, solid propylene carbonate, solid ethylene carbonate, solid t-butyl alcohol, solid t-amyl alcohol, cyclohexanol, phenol, and mixtures thereof. If such solids are in liquid form at ambient temperatures, they must not be a solvent for the ultra-high molecular weight polymer and should not be a contaminant or be incompatible with the hydrocarbon liquid or mixture for which drag reduction is desired. The grinding aid particles may be of any shape, but are typically crushed, or in the form of pellets or cubes. The grinding aid particles are preferably of equal size or smaller than the small polymer pieces and are more preferably between 1mm and 6mm (1/32 inch to 1/4 inch) in diameter. While the amount of grinding aid added is not critical, it is typically added so that the polymer/grinding aid mixture is between about 1% to about 5% by weight of the grinding aid by weight of the total mixture, with the balance being high molecular weight polymer. The use of the grinding aid allows reduction in the amount of partitioning agent required: In addition to the grinding aid, partitioning agent is typically added to pre-cooler 120. The amount of partitioning will vary depending on a number of factors, including the efficacy of a particular partitioning agent, the hydrocarbon in which the polymer will eventually be dissolved, and the polymer type itself. Generally, the amount of partitioning agent will be less than 50% of the total weight of the polymer/grinding aid/partitioning agent mixture, more frequently less than 35%. As those of skill in the art will appreciate, reducing the amount of partitioning agent will typically decrease the ratio of partitioning agent: polymer and reduce shipping weight. However,

as the partitioning agent acts to reduce agglomeration of polymer particles, reducing the concentration of partitioning agent below an appropriate level will make handling difficult. Nevertheless, formation of any multiple layer shell of partitioning agent around the polymer particles is undesirable and should be avoided where possible. Polymer added to pre-cooler 120 may be of larger-sized particles than that added to coarse chopper 110, for instance, small spheres or chunks, as long as the particles can be ground in the cryomill. Particle sizes of 25mm and larger may often be accommodated.

The final mixture of polymer/partitioning agent/grinding aid in the pre-cooler is typically: polymer 745% partitioning agent – <50%, frequently <3%; grinding aid about 10 1% to about 5%. Actual compositions will vary depending on particular conditions.

Pre-cooler 120 reduces the temperature of the small polymer pieces, partitioning agent, and grinding aid (“polymer mixture”) to a temperature below the glass transition temperature of the polymer. This temperature is preferably below -130°C (-202°F), and most preferably below -150°C (-238°F). These temperatures may be produced by any known methods, but use of a liquid refrigerant such as that consisting essentially of liquid 15 nitrogen, liquid helium, liquid argon, or a mixture of two or more such refrigerants sprayed directly onto the polymer is preferred, as the resulting atmosphere reduces or eliminates hazards that exist when polymer particles are mixed with an oxygen-containing atmosphere. The rate of addition of the liquid refrigerant may be adjusted to maintain the 20 polymer within the preferred temperature range.

After the polymer mixture is cooled in pre-cooler 120, it is transported to cryomill 130. Again, this transport may be accomplished by any typical solids handling method, but often by an auger or a pneumatic transport system. A liquid refrigerant may be added to

cryomill 130 in order to maintain the temperature of the ultra-high molecular weight polymer in cryomill 130 below the glass transition temperature of the ultra-high molecular weight polymer. The atmosphere within cryomill contains water vapor and oxygen from the ambient air. It is desirable to control the oxygen within cryomill 130 below 15% in order to reduce the risk of conflagration caused by grinding the polymer to dust-sized particles. In one embodiment of the invention, this liquid refrigerant is added to the polymer mixture at the entrance to cryomill 130. The temperature of the cryomill must be kept at a temperature below the glass transition temperature of the polymer. It is preferable to maintain the temperature of the cryomill between -130°C to -155°C (-202°F to -247°F).

10 Cryomill 130 may be any of the types of cryomills known in the art, such as a hammermill or an attrition cryomill. In an attrition cryomill, the polymer mixture is ground between a rapidly rotating disk and a stationary disk to form small particles between 10 and 800 microns in diameter.

The small particles formed in cryomill 130 are then transferred to separator 140.

15 Most of the liquid refrigerant vaporizes in separator 140. Separator 140 acts to separate the primarily vaporized refrigerant atmosphere from the solid particles, and the larger particles from the smaller particles. Separator 140 may be any known type of separator suitable for separating particles of this size, including a rotating sieve, vibrating sieve, centrifugal sifter, and cyclone separator. Separator 140 vents a portion of the primarily
20 vaporized refrigerant atmosphere from cryomill 130 and separates particles into a first fraction with less than about 400 microns in diameter from a second fraction of those with diameters of about 400 microns and above. The second fraction of those particles of about 400 microns and greater is discarded or preferably returned for recycle purposes to the pre-

cooler for re-grinding. The first fraction of those particles of less than about 400 microns is then transported to mix tank 150. The 400 micron size for the particles is nominal and may vary or have a distribution anywhere from about 100 to about 500 microns, depending on the separator, operating conditions, and desired end use.

5 While in particle form, care should be taken to keep the temperature of the small particles below the melt temperature of the grinding aid, and preferably below the glass transition temperature of the polymer. High temperatures will typically result in a reagglomeration of the polymer into a solid rubbery mass.

10 The small particles (the first fraction) are mixed with a suspending fluid in mix tank 150 to form a suspending fluid/polymer particles/grinding aid/partitioning agent mixture. The suspending fluid is any liquid that is a non-solvent for the ultra-high molecular weight polymer and compatible with the hydrocarbon fluid. Water is commonly used, as are other oxygenated solvents including some long chain alcohols such as isooctyl alcohol, hexanol, decanol, and isodecanol, low molecular weight polymers of ethylene or
15 propylene oxide, such as polypropylene glycol and polyethylene glycol, diols such as propylene glycol and ethylene glycol, and other oxygenated organic solvents such as ethylene glycol dimethyl ether and ethylene glycol monomethyl ether, as well as mixtures of these solvents and mixtures of these solvents and water. Mix tank 150 may be any type of vessel designed to agitate the mixture to achieve uniform composition of the suspending
20 fluid polymer particles mixture, typically a stirred tank reactor. Mix tank 150 acts to form a suspension of the polymer particles in the suspending fluid. The grinding aid particles may melt in the mix tank to mix with the carrier fluid or may dissolve. Other components may be added to the mix tank before, during, or after mixing the ground polymer particles

with the suspending fluid in order to aid the formation of the suspension, and/or to maintain the suspension. For instance, glycols, such as ethylene glycol or propylene glycol, may be added for freeze protection or as a density balancing agent. The amount of glycol added may range from 10% to 60% of the suspending fluid, as needed. A suspension

5 stabilizer may be used to aid in maintaining the suspension of the ultra-high molecular weight particles. Typical suspension stabilizers include talc, tri-calcium phosphate, magnesium stearate, silica, polyanhydride polymers, sterically hindered alkyl phenol antioxidants, graphite, and amide waxes such as stearamide, ethylene-bis-stearamide, and oleamide. Partitioning agent added in coarse chopper 110 and pre-cooler 120 will often

10 function as a suspension stabilizer as well. The total amount of partitioning agent/suspension stabilizer added may range from 0% to 40% of the suspending fluid, by weight, but is preferably between 5% and 25%, most preferably between 8% and 12%. A wetting agent, such as a surfactant, may be added to aid in the dispersal of the polymer particles to form a uniform mixture. Non-ionic surfactants, such as linear secondary

15 alcohol ethoxylates, linear alcohol ethoxylates, alkylphenol ethoxylates, and anionic surfactants, such as alkyl benzene sulfonates and alcohol ethoxylate sulfates, *e.g.*, sodium lauryl sulfate, are preferred. The amount of wetting agent added may range from 0.01% to 1% by weight of the suspending fluid, but is preferably between 0.01% and 0.1%. In order to prevent foaming of the suspending fluid/polymer particle grinding aid mixture during

20 agitation, a suitable antifoaming agent may be used, typically a silicon or oil based commercially available antifoam. Generally, no more than 1% of the suspending fluid by weight of the active antifoaming agent is used. Representative but non-exhaustive examples of antifoaming agents are the trademark of, and sold by, Dow Corning, Midland,

Michigan; and Bubble Breaker products, trademark of, and sold by, Witco Chemical Company, Organics Division. Mix tank 150 may be blanketed with a non-oxidizing gas such as nitrogen, argon, neon, carbon dioxide, carbon monoxide, gaseous fluorine, or chlorine, or hydrocarbons such as propane or methane, or other similar gases, or the non-oxidizing gas may be sparged into mix tank 150 during polymer particle addition to reduce the hazard of fire or explosion resulting from the interaction between the small polymer particles.

After the suspending fluid/polymer/particle mixture grinding aid is agitated to form a uniform mixture, a thickening agent may be added to increase the viscosity of the mixture. The increase in viscosity retards separation of the suspension. Typical thickening agents are high molecular weight, water-soluble polymers, including polysaccharides, xanthum gum, carboxymethyl cellulose, hydroxypropyl guar, and hydroxyethyl cellulose. Where water is the suspending fluid, the pH of the suspending fluid should be basic, preferably above 9 to inhibit the growth of microorganisms.

The product resulting from the agitation in the mix tank is a stable suspension of a drag-reducing polymer in a suspending fluid suitable for use as a drag-reducing agent. This suspension may then be pumped or otherwise transported to storage for later use, or used immediately.

The liquid refrigerant, as well as the suspending fluid, grinding aid, partitioning agent, detergent, antifoaming agent, and thickener, should be combined in effective amounts to accomplish the results desired and to avoid hazardous operating conditions. These amounts will vary depending on individual process conditions and can be determined by one of ordinary skill in the art. Also, where temperatures and pressures are

indicated, those given are a guide to the most reasonable and best conditions presently known for those processes, but temperatures and pressures outside of those ranges can be used within the scope of this invention. The range of values expressed as between two values is intended to include the value stated in the range.

CLAIMS

1. A method for the preparation of a drag-reducing polymer suspension comprising:
 - (a) mixing an ultra-high molecular weight polymer with a grinding aid to form
5 a polymer/grinding aid mixture with about 5% of less grinding aid, by total weight of the polymer/grinding aid mixture;
 - (b) mixing the polymer/grinding aid mixture with a partitioning agent to form a polymer/grinding aid/partitioning agent mixture;
 - (c) grinding the polymer/grinding aid/partitioning agent mixture in the presence
10 of oxygen or water vapor at a temperature below the glass-transition temperature of the ultra-high molecular weight polymer to form ground polymer particles; and
 - (d) mixing the ground polymer particles with a suspending fluid to form the drag-reducing polymer suspension.
2. The method as described in claim 1, wherein the ultra-high molecular weight
15 polymer comprises a linear poly(α -olefin) produced from one or more α -olefin monomers with carbon chain lengths of between 4 and 20 carbons, or mixtures of two or more such linear poly(α -olefins).
3. The method as described in claim 1, further comprising prior to step (a): cooling
20 the ultra-high molecular weight polymer with one or more refrigerants selected from the group consisting of liquid nitrogen, liquid helium, liquid argon, and dry ice.
4. The method as described in claim 3, further comprising prior to or simultaneously with step a):
cooling the ultra-high molecular weight polymer to a temperature below -130°C
- 25 5. The method as described in claim 1, wherein the grinding aid has a melting point of between -100°C to 25°C .

6. The method as described in claim 5, wherein the grinding aid is selected from the group consisting of ice, sucrose, glucose, lactose, fructose, dextrose, sodium saccharin, aspartame, starches, solid propylene carbonate, solid ethylene carbonate, solid t-butyl alcohol, solid t-amyl alcohol, cyclohexanol, phenol, and mixtures thereof.

5 7. The method of claim 1 further comprising after step a) and before step b):

separating the ground polymer/grinding aid particles into a first fraction with a diameter of less than 400 microns from a second fraction of the ground polymer/grinding aid particles with a diameter of 400 microns or greater; and

10 regrinding the second fraction of the ground polymer/grinding aid particles with a diameter of 400 microns or greater.

8. The method of claim 7, wherein the suspending fluid comprises water or an oxygenated organic solvent.

9. The method of claim 8, wherein the suspending fluid further comprises a suspension stabilizer.

15 10. The method of claim 8, wherein the suspending fluid further comprises one or more components selected from the group consisting of a detergent, an antifoaming agent, and a thickening agent.

11. A method for the preparation of a drag-reducing polymer suspension comprising:

20 a) cooling an ultra-high molecular weight polymer with one or more refrigerants selected from the group consisting of liquid nitrogen, liquid helium, liquid argon, and dry ice, wherein the ultra-high molecular weight polymer produced from linear poly(α -olefin) comprised of α -olefin monomers with carbon chain lengths of between 4 and 20 carbons, or mixtures of two or more such linear poly(α -olefins);

25 b) mixing the ultra-high molecular weight polymer with a grinding aid to form a polymer/grinding aid mixture with less than about 5% grinding aid as a percent of the total mixture weight;

c) grinding the polymer/grinding aid mixture at a temperature below the glass transition temperature of the polymer while within an atmosphere comprising oxygen or water vapor;

d) mixing the ground polymer/grinding aid mixture particles with a suspending fluid, the suspending fluid further comprising one or more components selected from the group consisting of adding a wetting agent, an antifoaming agent, and a thickening agent.

12. The method as described in claim 11, wherein the grinding aid has a melting point of between -100°C to 25°C .

10 13. The method of claim 11, wherein the grinding aid is selected from the group consisting of ice, sucrose, glucose, lactose, fructose, dextrose, sodium saccharin, aspartame, starches, solid propylene carbonate, solid ethylene carbonate, solid t-butyl alcohol, solid t-amyl alcohol, cyclohexanol, phenol, and mixtures thereof.

15 14. The method of claim 11, wherein the suspending fluid comprises water or an oxygenated organic solvent.

15. The method of claim 11, wherein the suspending fluid further comprises a suspension stabilizer.

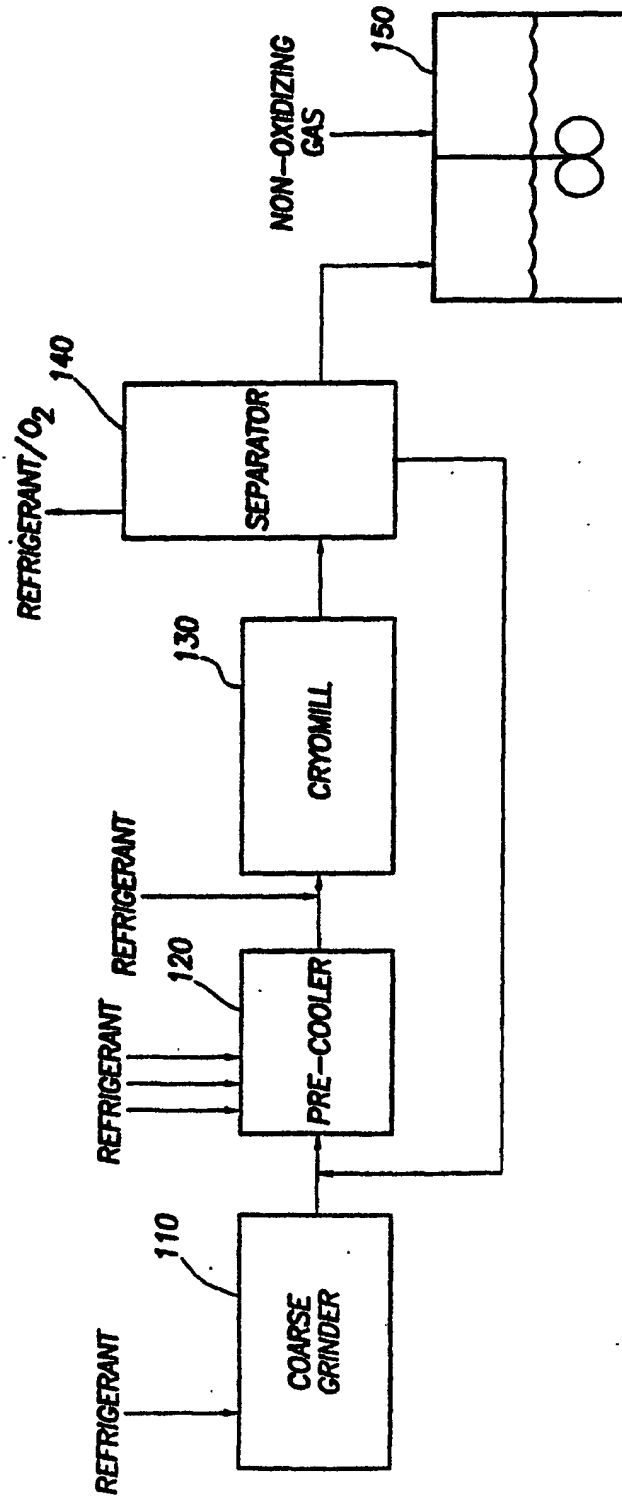


FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/30815

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08J3/05 C08J3/12 B02C19/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J B02C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 539 044 A (MASSOUDA DEBORA F ET AL) 23 July 1996 (1996-07-23) the whole document	1-15
X	WO 97 32926 A (CONOCO INC) 12 September 1997 (1997-09-12) the whole document	1-15
X	US 5 244 937 A (ADAMS WILL G ET AL) 14 September 1993 (1993-09-14) the whole document	1-15
A	US 3 771 729 A (FRABLE N) 13 November 1973 (1973-11-13) the whole document	1-15
-/-		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 273 294 A (HOLLELY DAVID J E ET AL) 16 June 1981 (1981-06-16) the whole document	1-15
A	US 4 826 728 A (O'MARA DION P ET AL) 2 May 1989 (1989-05-02) the whole document	1-15
A	US 3 636 136 A (KONOPIK ALVIN E) 18 January 1972 (1972-01-18) column 4, line 22 - line 48	1,6,11, 13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/30815

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5539044	A	23-07-1996	CA 2247100 A1 WO 9732926 A1 EP 0885259 A1 NO 984113 A	12-09-1997 12-09-1997 23-12-1998 09-11-1998
WO 9732926	A	12-09-1997	CA 2247100 A1 US 5539044 A WO 9732926 A1 EP 0885259 A1 NO 984113 A	12-09-1997 23-07-1996 12-09-1997 23-12-1998 09-11-1998
US 5244937	A	14-09-1993	AU 649371 B1 CA 2098221 A1 EP 0626418 A1 FI 932123 A NO 931710 A AT 170893 T DE 69320943 D1 DE 69320943 T2 DK 626418 T3 ES 2121894 T3	19-05-1994 12-12-1994 30-11-1994 12-11-1994 14-11-1994 15-09-1998 15-10-1998 04-02-1999 22-02-1999 16-12-1998
US 3771729	A	13-11-1973	CA 985665 A1 DE 2223769 A1 FR 2142523 A5 GB 1340312 A IT 957727 B ZA 7201507 A	16-03-1976 21-12-1972 26-01-1973 12-12-1973 20-10-1973 25-04-1973
US 4273294	A	16-06-1981	GB 2044126 A BR 8001553 A CA 1149357 A1 DE 2964039 D1 EP 0017368 A1 MX 149975 A ZA 8001490 A	15-10-1980 11-11-1980 05-07-1983 23-12-1982 15-10-1980 21-02-1984 25-03-1981
US 4826728	A	02-05-1989	US 4720397 A AT 87511 T AU 595300 B2 AU 7021487 A CA 1315160 A1 DE 3688200 D1 DE 3688200 T2 DK 416387 A EP 0289516 A1 JP 7068356 B JP 1500357 T NO 873346 A ,B, NO 912565 A ,B, WO 8703516 A1 US 4789383 A US 4837249 A US 4758354 A	19-01-1988 15-04-1993 29-03-1990 30-06-1987 30-03-1993 06-05-1993 21-10-1993 12-10-1987 09-11-1988 26-07-1995 09-02-1989 12-10-1987 12-10-1987 18-06-1987 06-12-1988 06-06-1989 19-07-1988
US 3636136	A	18-01-1972	DE 2056788 A1 FR 2069543 A5 GB 1329741 A	27-05-1971 03-09-1971 12-09-1973

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/30815

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3636136	A	JP 48011222 B	11-04-1973